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EXPLORATORY DEVELOPMENT OF CONDUCTIVE COATING MATERIALS

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This report covers the work from March 15, 1976 to March 15, 1977.

This report has been reviewed by the Information Office (ASK/OIP) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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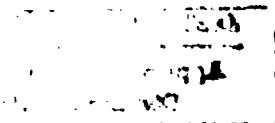
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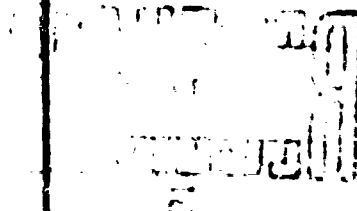
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flocculation was with an applied electric field. With the flocs thus formed, they were cemented into permanent units with a SiCl_4 treatment. The second problem examined was the preparation of a white pigment with a stable conductance showing resistance to oxidation. It is pointed out that more work on this latter problem is needed before a completely satisfactory paint is developed.

Conductive white radome coatings are needed to protect USAF aircraft radomes in a thermal flash environment. A highly reflecting white pigment in a radome coating will reflect most of the visual and infrared wavelength, incident energy in a thermal flash environment. Nonconductive radome coatings build up a static charge as the radome is propelled through the air. A conductive coating provides a path for dissipation of the static charge. The use of white conductive coatings on radomes will provide for the satisfactory use of USAF aircraft radars in normal operational, environment and hostile thermal flash environment.



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I INTRODUCTION AND SUMMARY

The overall goal of this program has been to prepare a stable, erosion-resistant, white conducting coating, based on titanium dioxide (TiO_2), zinc oxide (ZnO), or tin oxide (SnO_2) pigments with a fluoro-carbon or polyurethane binder. The pigment volume concentration (PVC) must be low for erosion resistance, and the pigment must be made to conduct in a way that leads to stability against the effects of oxygen in air. Thus, the program has two specific objectives. The first is to establish continuous conducting paths at low PVC, by controlling flocculation to simulate that of carbon-based paints (namely to induce a "snowflake" or "lacework" floc structure). With such a structure, continuous particle-to-particle conducting paths through the coating will be present while retaining an open structure for a low PVC and hence good erosion resistance. The second objective is to develop doping techniques such that the conducting pigment will be resistant to slow oxygen adsorption.

The approach we have been taking entails several steps:

- (1) Determine how to induce chain flocculation of the pigments.
- (2) Determine how to stabilize the chains to prevent their destruction during dispersion in a paint vehicle.
- (3) Using the chain flocs, formulate and test a conductive paint of low PVC.
- (4) Determine the optimum technique for donor and surface additive incorporation using best results obtained in steps (1) and (2).
- (5) Determine how best to stabilize the conductivity against slow oxygen adsorption.

We have emphasized (1) and (2) in the present research, working on both problems simultaneously. It was considered desirable to complete (1) and (2) before initiating (4) and (5), because with favorable flocculation an improved coating can be formulated immediately using standard methods. Steps (4) and (5) represent another distinct improvement, best taken now that (1) and (2) are satisfactorily completed. In the present summary we discuss our work in the order shown in the above listing, as this order is logically clearer. In the detailed technical report, Section II, however, we first discuss the work on step (2), studies of coupling agents, and then the work on flocculation, because the approaches chosen for flocculation were determined by the results of the coupling agent studies.

Chain Flocculation

Several methods were tried to induce chain flocculation of the pigments, both with the pigment present in a liquid suspension and with the pigment introduced as an aerosol. These methods are described briefly here and in detail in Section IIB.

Zeta Potential Studies

To cause chain flocculation in a liquid suspension, it was clear that an accurate control over the zeta (ζ) potential of the particles was needed. The ζ potential particularly in an aqueous solution but to a great extent in a nonaqueous solvent as well, is associated with a double layer that arises at the surface of the particles and that keeps the particles from flocculating.

According to the literature,¹ chain flocculation should occur if the ζ potential is controlled to be in a very narrow range of values. To induce chain flocculation directly by such ζ potential control, the approach¹ is to lower the ζ potential to the point of very slow flocculation.

At this ζ potential value, by theory the flocculation should be in the form of chains. Then when the chains have grown to the desired length, the concept is to make the ζ potential high and, thus, stop further flocculation of the material.

With other means of chain flocculation, such as the use of an electric field, ζ potential is still needed to avoid general flocculation. In other words, we want the ζ potential high, so the pigment particles will not flocculate, but low enough that the imposed force, the electric field, will just suffice to cause chain flocculation. Then unwanted flocculation will not occur. Thus, in any method of inducing chain flocculation in a liquid, some control over the ζ potential is desirable. Therefore, we have spent some effort in studies of the ζ potential of pigment particles and its control, studying not only the use of additives to change the ζ potential and, thus, induce flocculation, but also the direct measurement of ζ potential itself.

Electric Field Induced Flocculation

The use of an electric field at a fine wire or at a knife edge to attract the pigment particles by dielectrophoresis was identified as the most direct way to induce chain flocculation. We have not eliminated the use of other methods, and at some future time it may be desirable to return to other techniques of inducing chain flocculation (such as directly by ζ potential control) because the rate of chain flocculation at a fine wire or at a knife edge is of necessity relatively low. However, for the limited quantities of paint needed for present purposes, the rate seems satisfactory, and because the method is direct and satisfactory we have continued in this direction.

Dielectrophoresis is the attraction of pigment particles using an ac electric field, usually a nonuniform electric field (see the theoretical discussion in Section IIB). Because the pigments of interest have a very

high dielectric constant, they are attracted to the high field region, the attraction being independent of the sign of the field and, thus, independent of any electrostatic or electrophoretic effects. The use of an ac electric field, depending on the dielectrophoresis effect, thus avoids problems due to undesired electrostatic charging of pigment particles.

We have obtained satisfactory chain flocculation with a high ac voltage applied to a knife edge introduced into a slurry of pigments particles in a nonpolar solvent or to a fine (0.003 inch) wire introduced into an aerosol of pigment particles in air or nitrogen. The particles sometimes form branched chains and show the snowflake or lacework structure desired for the present purpose.

Stabilization of the Chain Flocs

Once the flocs are formed, either at the surface of a wire from a gaseous aerosol or at knife edge from a liquid solvent, it is desired to bond or cement the particles to make the chain structure in the floc permanent. The object is to promote enough bonding so that the chains can be removed from the wire or knife edge and introduced into a vehicle without destroying their open structure, even if light milling is required. The method we adopted to try to cement the particles together while on the knife edge or on the wire is to use bifunctional coupling agents to bridge between particles, with one functional group attached to each of the adjacent particles. The behavior of many coupling agents at the tin oxide, zinc oxide, and titanium oxide surfaces were tested and two approaches were selected that provide good bonding strength to the chains, one useful in a liquid solvent and one in an aerosol.

In the case of chains formed in a liquid solvent, a titanium phosphate bridging agent that could form a permanent bond at room temperature

was selected as optimum. However this liquid-phase/titanium phosphate approach has not been studied in detail. The use described below of the gas phase technique for chain production in an aerosol was highly developed by the time the titanium phosphate bridging agent was identified. It was concluded at that time that the most direct solution to the overall problem would be reached by concentrating on the gas-phase approach to chain floc generation.

The coupling agent identified for use in the gas-phase work was tetrachlorosilane (SiCl_4) which, when introduced at high temperature (about 400°C or higher), induced substantial strengthening of the inter-particle contacts.

Generation of Stabilized Chain Flocs

An apparatus was constructed for the preparation of chain flocs from an aerosol and the simultaneous or subsequent exposure of these chain flocs to tetrachlorosilane as the bonding agent. It was found in separate experiments that the preferred method of removal of the chain flocs from the wires was a mechanical approach--simply scraping the chain flocs from the wire. Thus, the apparatus, as finally developed, includes a gridwork of wires to form the chain flocs from an aerosol passing by; facilities for the introduction of tetrachlorosilane to adsorb onto chain flocs; facilities for heating the wire to 400°C , or substantially higher, to induce a bridging reaction of the tetrachlorosilane; and, finally, facilities for moving the wires through a scraper and allowing the chain flocs to drop into a collecting hopper. All of these functions can be done automatically.

As the final phase in the current program, the use of conductive titanium dioxide in generation of chain flocs was explored to determine whether specific problems associated with the conductivity arose. It

was found that the conducting titanium dioxide behaved rather better than the insulating titanium dioxide--the form of the chain flocs was more linear and more insensitive to the exact electric field applied, and the introduction of the tetrachlorosilane substantially increased the interparticle conductance.

Future Work Needed

Before a usable paint is available, several steps must still be taken. Large batches of chain flocs must be prepared, sufficient for the development of satisfactory flow and settling properties of the paint, and sufficient for the development of satisfactory film-conductance properties in the paint. Additives to control the settling of the chains must be introduced, and the conditions required with respect to chain size must be explored to satisfy the stability requirement. With large quantities of pigment available, we can more easily study the control of the conductive properties of the paint and develop appropriate bulk and surface treatments for the pigment itself. The problems anticipated include establishment of the desired initial conductance and also prevention of the slow oxidation of the pigment particles leading to the removal of electrons from the particles and, thereby, a slow decrease in interparticle conductivity.

II EXPERIMENTAL PROGRAM

A. The Addition of Coupling Agents to form Interparticle Bonds

1. Development of Methods of Testing Bonding Strength

Although there has been a report in the literature² that coupling agents added to pellets of oxide materials tend to form an intergranular bond between the oxides, only qualitative observations were made, and no quantitative tests have been developed. Thus, we were required to develop our own testing methods concurrently with the development of techniques for depositing the coupling agents. Several testing techniques were examined. Three methods were considered for determining whether strengthening occurred when the coupling agent was added to pigment agglomerates, and two methods were examined for determining whether strengthening occurred when the coupling agent was deposited on pressed pellets of the pigment.

Sand milling as a test of the strength of agglomerates showed no significant ability to distinguish the effective coupling. Unfortunately, the sand milling test was examined very early in our studies, and it was found later that at that early time the techniques for addition of the coupling agents had been ineffective, so the sand milling tests were not given a fair evaluation. In the tests, the agglomerated pigment is introduced into a sand mill, and the particle size of the emerging particles is examined microscopically. If the coupling agent is effective, the particle size would be larger than in the corresponding untreated powder.

Another technique tested for measuring the hardness of agglomerates is the pressure/volume relationship as measured in an Instron

machine. Here the concept is that if the treated agglomerates have an unusually high strength, substantially higher pressure should be required on the Instron machine to compress a pellet of a given dimension. Unfortunately, in these studies it was found that the difference between a treated and untreated material was insufficient to provide a reliable discrimination.

The test found finally to distinguish successfully the strength of coupling when the coupling agent is applied to an agglomerated pigment is a screening test. In this test a certain screen fraction is initially selected. After treatment with the coupling agent, the powder is returned to the screen and mechanically vibrated. The rate of which the particles are further fractured simply by abrasion against the screen is found to give a satisfactory indication of the strength of the material. Tests of harder materials can be made by adding glass balls to the powder to provide more forcible abrasive action. As will be discussed below, a significant reduction in the rate of abrasion of the agglomerates over the rate for a blank is observed following pretreatment with a successful coupling agent.

Two testing techniques were investigated in which the pigment was pressed into a pellet before exposure to the coupling agent. One was fracture of the pellet, but it was found that the force necessary for fracture was much too irreproducible to provide a suitable hardness test. The second, which was found reasonably reliable and is the basis for many of the studies reported below, was the measurement of hardness using a diamond point, the Vickers hardness test. In this test, a diamond of pyramid shape is pressed into the surface of the pellet with a definite force (usually the order of 100 grams), and the depth of penetration of the diamond is determined by measuring the width of the imprint under a microscope.

2. Addition of Coupling Agents from Solution: High Temperature Curing

Studies were made on the possibility of bridging pigment particles in a slurry using alkoxide titanate ester compound, with a titanium ester diphosphoric acid, and with a dichlorosilane and various dichlorosiloxanes as the coupling agents. The results as described below were unsatisfactory compared to the methods later developed, reported in subsections 3 and 4 below. The pigments used in these studies were titanium (IV) oxide (Zopaque R-88 from Glidden) zinc oxide (SP-500 from New Jersey Zinc), and tin (IV) oxide (Alfa Products). Treatments were made in solvents such as dry methylethyl ketone (MEK), dry xylene, and dried tetrahydronaphthalene (Tetralin). Treatments in MEK and in xylene were made at room temperature. Treatments in tetralin were made at reflux temperature, 207°C. Table 1 summarizes the results of our studies in liquid-phase addition of coupling agents. In particular, the table gives the sedimentation time after treatment to indicate whether adsorption of the coupling agent occurred. The details of the various treatments are given in the sections below.

a. The Adsorption of Titanium Phosphate Coupling Agent

One of the bridging experiments entailed an attempt to tie titanium (IV) oxide pigment particles together through an alkyd ester by means of transesterification with the phosphate function of an isopropyl tri (diisooctyl phosphate) titanate (TTOP-13). 18 g R-88 rutile and 120 g Ottawa sand, ASTM C190-20-30 mesh, were loaded into a ceramic jar and dried for 2 hours at 200°C. After cooling, 39.6 g dry MEK and 3 drops of oleic acid were added. The jar was closed, and the contents shaken for 1-1/2 hours in a Red Devil paint shaker. The sand was then filtered off, and a dispersion of TiO_2 in MEK was obtained (I). A similar dispersion (II) was prepared without the oleic acid addition. Four test samples were then prepared from these dispersions as in Table 2.

Table 1

COMPARISON OF SEDIMENTATION TIMES (t) FOR SEVERAL PIGMENTS IN NONAQUEOUS MEDIA

Pigment	Solvent	Coupling Agent		t (s) (min)	Experimental Procedure	
		Type	Amount in Moles/g Pigment		Experimental Number	Formulation Number
TiO ₂	MEX	None	$1/2 \times 10^{-4}$	300 to 14.2 ml	1	Control
TiO ₂	MEX	TTOP-12 (W/MC-258)	$1/2 \times 10^{-4}$	200 to 14.2 ml	1	1
TiO ₂	MEX	TTOP-12 (W/MC-258)	$1/2 \times 10^{-4}$	180 to 14.2 ml	1	2
TiO ₂	MEX	TTOP-12 (W/MC-258)	1×10^{-3}	20 to 14.2 ml	1	3
TiO ₂	MEX	TTOP-12 (W/MC-258)	1×10^{-4}	50 to 14.2 ml	1	4
TiO ₂	MEX	None	-	300 to 14.2 ml	22	Control
TiO ₂	MEX	TTOP-12 Chlorocathylmethyl dichlorosilane	$1/2 \times 10^{-4}$	2 to 14.2 ml	2	-
ZnO	MEX	None	-	90 to 14.2 ml	3	Control
ZnO	MEX	Chloromethylmethyl dichlorosilane	$1/2 \times 10^{-5}$	90 to 14.2 ml	3	-
ZnO	MEX	None	-	3.5	4	1
ZnO	MEX	1,8-Di chlorohexamethyl trisiloxane	1×10^{-4}	0.3	4	2
ZnO	MEX	None	-	>12	4	3
ZnO	MEX	1,8-Di chlorohexamethyl trisiloxane	1×10^{-4}	>15	4	4
ZnO	MEX	None	-	10 to 7.6 ml	4	5
ZnO	MEX	1,8-Di chlorohexamethyl trisiloxane	1×10^{-4}	3 to 7.6 ml	4	6
ZnO	MEX	1,8-Di chlorohexamethyl trisiloxane (W/pyridine)	$1/4 \times 10^{-4}$	15 to 10 ml	6	1
ZnO	MEX	1,8-Di chlorohexamethyl trisiloxane (W/C pyridine)	$1/4 \times 10^{-4}$	15 to 10 ml	6	2
SnO ₂	Xylene and tetralin	None	-	4 to 10 ml	7	Control
SnO ₂	Xylene and tetralin	Chlorotrimethylsilane	$1/3 \times 10^{-4}$	3 to 10 ml	7	
SnO ₂	Tetralin	1,5 Di chlorohexamethyl	$2/3 \times 10^{-4}$			

(t) Time for pigment in 10-ml slurry to settle to about 3 ml or to an amount in ml as noted.

Table 2

TEST SAMPLE FORMULATION PROCEDURE

	<u>Control</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
TiO ₂ Dispersion (I)	9.0	9.0	-	9.0	9.0
TiO ₂ Dispersion (II)	-	-	9.0	-	9.0
Dry MEK	20 ml	20 ml	20 ml	20 ml	20 ml
Sorbitan Monolaurate (Span 20, Atlas Chemical Co.)	3 drops	3 drops	-	3 drops	-
The above was shaken for 10 min on a paint shaker, then the following was added:					
Dupont RC 288	1.5	1.5	1.5	1.5	1.5
Dry MEK	20 ml	20 ml	20 ml	20 ml	20 ml
Following the second addition, the contents were shaken for 1 hour on a paint shaker. The following was then added:					
TTOP-12	-	0.16	0.16	0.32	0.32

Note: Test formulations are in grams or as noted.

After TTOP-12 addition, the formulations were stirred for 23 hours in a closed container using a laboratory magnetic stirrer. They were then tested for sedimentation and were microphotographed after having been further diluted with MEK. It was found that the treated TiO_2 formed slightly larger particles, as seen under the microscope, and settled somewhat faster in the sedimentation test when compared with tests on the untreated oxide. Although these results are in the desired direction, we cannot be certain that the strength of the agglomerated particles increased. Sedimentation times are shown in Table 1.

b. Chlorosilanes as Coupling Agents

A second bridging experiment entailed an attempt to tie TiO_2 pigment particles together by means of a dichlorosilane, chloromethyl methyl dichlorosilane. In this experiment, half of the reactive TiOH surface sites were prereacted with a monofunctional coupling agent, TTOP-12, and the remainder of the sites with the dichlorosilane. A ceramic jar was loaded with 12 g R-88 rutile and 80 g Ottawa Sand, 20-30 mesh, and dried for 2 hours at 200°C . After cooling, 26.4 ml dry MEK and 2 drops oleic acid were added. The jar was closed and shaken for 1-1/2 hours in a Red Devil paint shaker. The sand was then filtered off to obtain the TiO_2 dispersion in MEK. 9 g of this dispersion was mixed with 20 ml dry MEK and 3 drops of Span 20. This was shaken on the paint shaker for 10 minutes. TTOP-12 (0.16 ml) was then added, and the dispersion stirred for 1 hour with a magnetic stirrer. Then 0.04 ml chloromethylmethyl dichlorosilane was added, and the dispersion stirred for an additional hour. It was found that the treated titanium (IV) oxide formed much larger agglomerates than the control on microscopic examination and settled much faster than the control in the sedimentation test. However, the treated TiO_2 was not tested for agglomerate strength. Sedimentation times are shown in Table 1.

In the third experiment, an attempt was made to bridge ZnO pigment particles together by means of the dichlorosilane, chloromethylmethyl dichlorosilane. The procedure followed is identical to that described for the second experiment involving titanium (IV) oxide. The treated sample showed almost identical results to that of the control when tested by sedimentation rate and on the microphotographic studies of agglomeration. Therefore, we conclude that no bridging has occurred.

c. Siloxane as a Coupling Agent

A fourth set of experiments was performed using 1,5 dichlorohexamethyltrisiloxane as a coupling agent for bridging metal oxide particles with the hope of improvement by having separation between functional groups in the coupling agent molecule. In these experiments the amount of coupling agent was varied, and the dispersion time, using sand as the dispersing agent, was also varied if the vigorous 1-1/2 hour mechanical agitation used in Experiment 3 was cleaving the chemical bonds of coupling agent to zinc oxide particles. All ingredients used in these experiments were dried as previously described, i.e., pigment and sand at 200°C for 2 hours, and MEK dried over calcium hydride. Samples were prepared as listed in Table 3.

The sedimentation time of these formulations is shown in Table 1. These results show that the 1-1/2 hour sand dispersion causes agglomerates to be broken up. They also show that the dichlorosiloxane treatment, when not accompanied by the sand dispersion step, gives faster settling time. Predispersion of pigment, such as in Formulations 5 and 6, resulted in a lesser relative speed of settling as compared to the use of undispersed pigment. The microphotographs bore out the conclusion that the 1-1/2 hour sand dispersion used in Formulations 3 and 4 separated agglomerates into small particles.

The fifth experiment entailed a study on the effect of mixing time on zinc oxide dispersions coupled with 1,5-dichlorohexamethyl

Table 3

PREPARATION OF SAMPLES FOR SILOXANES BRIDGING TESTS

Ingredient and Procedure	Formulation Number					
	1	2	3	4	5	6
ZnO	1.5 g	1.5 g	1.5 g	1.5 g	-	-
MEK	20 ml	20 ml	20 ml	20 ml	20 ml	20 ml
1,5-Dichlorohexameth- yltrisiloxane	-	0.0416	-	0.0416	-	0.0526 ml
ZnO Dispersion*	-	-	-	-	5.0	5.0
Procedure	Not shaken or depressed.	Same as for 1.	Shaken 1-1/2 hr with sand on paint shaker.	Same as for 3.	Same as for 1.	Same as for 1.

*50 g ZnO plus 100 ml MEK. Ball milled 16 hours.

trisiloxane. The formulations were sand milled for various times up to 10 minutes, and the sedimentation results noted. The sediment (in ml) after 10 minutes of settling is shown in Table 4.

It is obvious from the results of Table 4 that although the sampling agent speeds up the settling time, sand milling leads to agglomerate breakup with slower settling times.

d. Use of a Catalyst

There is evidence from our gas-phase work that dichlorosilanes require a temperature of over 200°C to effect good coupling with the reactive surface Sn-OH sites. It is likely that similar temperatures might be required with zinc oxide and titanium (IV) oxide. Our experiments with dichlorosilanes and dichlorosiloxanes were done at room temperature. A sixth set of experiments was performed in an attempt to determine if there was evidence of room-temperature catalytic enhancement of coupling using pyridine as the catalyst. The formulations were as follows:

	<u>Formulation No.</u>	
	<u>1</u>	<u>2</u>
ZnO	1.5 g	1.5 g
MEK	20 ml	20 ml
1,3-Dichlorohexamethyl trisiloxane	0.0105 ml	0.0105 ml
Pyridine	0.002 g	0.002 g

Essentially no difference was found in the sedimentation time of the two formulations, nor were there any marked differences between the microphotographs. Sedimentation times are shown in Table 4.

Table 4

FORMULATION OF ZINC OXIDE DISPERSIONS FOR TRISILOXANE COUPLING

Formulation Number	Mixing Time with Sand in Paint Shaker (min)			
1 ^(a)	0	1	3	10
ml of sediment after 10 min settling time	2.8	11.0	10.5	9.5
2 ^(b)				
ml of sediment after 10 min settling time	0.7	4.5	4.8	4.4
(a) Formulation of : ZnO	7.5 g			
MEK	100 ml			
(b) Formulation: ZnO	7.5 g			
MEK	100 ml			
1,5 dichlorohexamethyl trisiloxane	7.5×10^{-4} moles			

e. Use of High-Temperature Solvents

The seventh experiment was designed to couple tin (IV) oxide with 1,5-dichlorohexamethyl trisiloxane by reflux in tetralin, bp 207°C. All solvents were predried over sodium and distilled. Three grams of tin (IV) oxide were added to 100 ml xylene. Then, 0.0972 g of chlorotrimethyl silane was added, and the xylene mixture was refluxed for 2 hours. Then, 100 ml of tetralin was added along with 0.021 ml of dichlorohexamethyl trisiloxane, and reflux was continued for 2 hours, with water and xylene separation being effected by the use of a Dean Stark trap. A control sample run was prepared in exactly the same way but without coupling agent. The sedimentation time for the coupled tin (IV) oxide particles was slightly faster than that of the control. Sedimentation results are shown in Table 1.

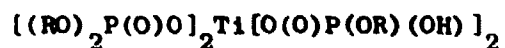
Another experiment was designed to answer the question of whether the 1,5-dichlorohexamethyl trisiloxane, which has a boiling point of 148° at 760 mm, was lost at the reflux temperature of the boiling tetralin, at 207°C. The next higher homolog, 1,9-dichlorodecamethyl pentasiloxane, was prepared using the partial hydrolysis method of Patnode and Wilcock.³ This compound has a boiling point of 138°C at 20 mm or above that of the tetrasiloxane, which has a boiling point of 222° at 760 mm and 111°C at 20 mm. This was used to couple rutile titanium (IV) oxide by the following procedure.

Five grams of rutile, R-88 from Glidden, was added to 100 ml of tetralin in a 250-ml round-bottom flask and refluxed for 18 hours, and the water was collected in a Dean Stark trap. 0.212 g of 1,9-dichlorodecamethylpentasiloxane was added and reflux continued for 2 hours. The tetralin was decanted off, after cooling, and the solids were washed four times with methylene chloride. It was then air dried and submitted to a screening test for agglomerate strength. However,

because of the dispersion of the original agglomerate of TiO_2 particles into small individualized particles during the reflux operation, no meaningful mechanical strength measurements could be made.

3. Addition of Titanium Phosphate Coupling Agents Using a Room-Temperature Cure

Another set of experiments involved the possibility of coupling surface metal hydroxide groups with a diphosphoric acid functional compound, titanium (IV) bis[(di-2-ethylhexy) orthophosphate] bis [(mono-2-ethylhexy) orthophosphoric acid] also known as "Thiphos." This compound is available from Research Organic/Inorganic Chemical Corporation and has the following structure:



where R = 2-ethylhexyl.

We were interested in the possibility of coupling Thiphos to the pigment at room temperature. In the first experiment, 5 g of titanium (IV) oxide, R-88, of 24-32 mesh agglomerate size, was dried in a flask for 2 hours at 200°C. It was then stoppered and cooled. One gram of Thiphos was added to the TiO_2 along with 75 ml sodium-dried xylene. The slurry was stirred for 2 hours with a magnetic stirrer. After standing overnight, the solvent was decanted off, and the rutile washed four times with methylene chloride and then air dried. The agglomerate size remained unchanged as a result of these operations. The dried sample was subjected to a screening test for agglomerate strength.

The screening test indicated significant improvement in the agglomerate strength resulting from the presence of the coupling agent. Without the coupling agent, 85% of the powder was retained in the screen; with the coupling agent, 95% of the powder was retained after a 5-min treatment.

With this encouraging result, an improved test adapted to the liquid system based on the Vickers Hardness method was developed.

Titanium (IV) oxide and/or zinc oxide pellets were pressed into pellets of 1.27-cm diameter and 0.20-cm thickness at 6,000 psi. The pellets were immersed for 16 hours in xylene containing 1×10^{-4} moles of coupling agent per gram of pigment. The solution was then decanted off and the pellets were air-dried for 18 to 24 hours prior to testing. Controls, containing no coupling agent, were run in a like manner. The tin (IV) oxide pellets were rendered so fragile by the treatment that breakage occurred on subsequent handling. Therefore, the bulk of the tests were performed on the less fragile zinc oxide pellets. However, because the solvent soak decreased the hardness of the zinc oxide pellets to some degree, comparisons of coupling agent effectiveness were made against results obtained with solvent-exposed control samples.

This weakening of the pellets by solvent immersion, although awkward at this stage of testing, will not be a handicap during chain formation and cementing. During the real process, the particles, while in the liquid, are forced together by the electric field; simultaneously, the coupling agent acts to cement the interparticle contacts. Thus, the strengthening reported below is the important observation--the weakening of pellets by immersion has no bearing on the proposed system.

Studies were made using the above measurement technique on the possibility of bridging pigment particles not only with a titanium (IV) bisphosphate bisphosphoric acid compound (Thiphos, from Research Organic/Inorganic Corporation) but also with several new polyfunctional titanium phosphato and phosphito coupling agents supplied by Kenrich Petrochemicals, Inc.

Zinc oxide pellets treated with tetraisopropyl di(Diisopropylphosphito) titanate were found to give the highest Vickers hardness readings. Treatments with tetra(2,2-diallyloxymethyl-1-butenoxy) titanium di(ditridecyl phosphite) also produced high hardness measurements, and treatments with titanium di(dibutylpyro-phosphate) oxyacetate and tetraoctyloxy titanium di(Dilauryl-phosphite) produced a small increase in hardness. Thiphos-treated samples showed little or no change in intergranular strength or conductance. The hardness values for the other previously listed treatments are shown in Table 5.

4. Addition of Coupling Agents from the Gas Phase

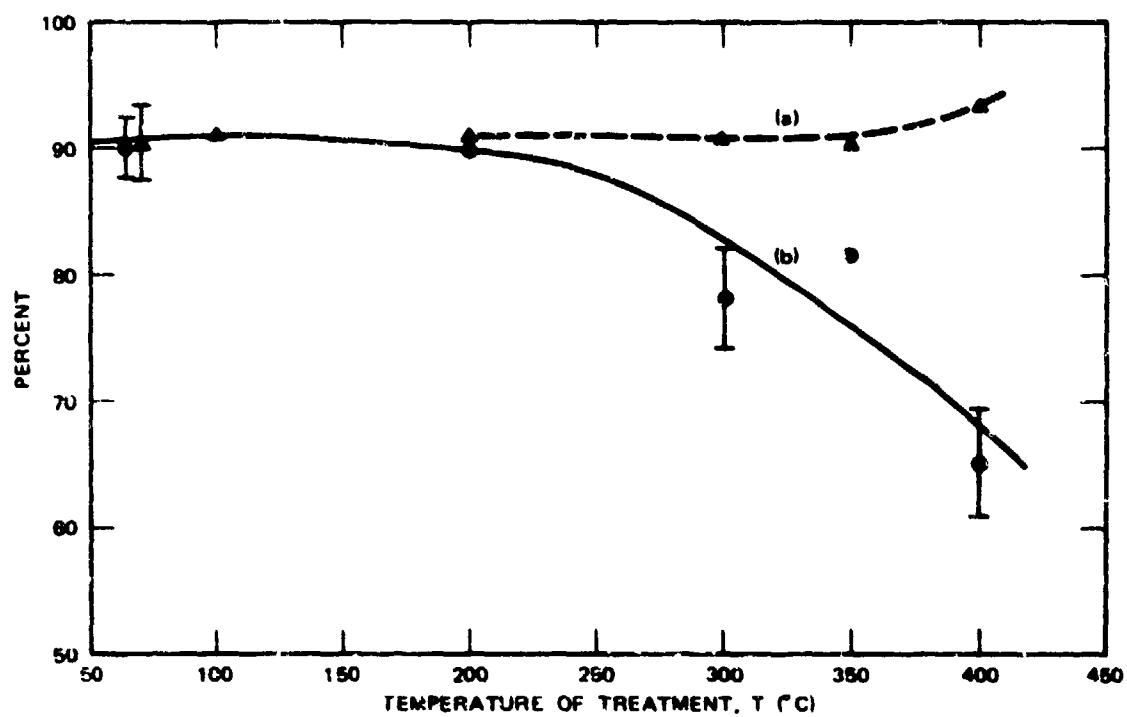
Two techniques have been used to deposit coupling agents onto pigments from the gas phase; the first with the coupling agent conveyed by a carrier gas such as nitrogen or air, the second with the coupling agent admitted to an evacuated sample chamber. The first technique is clearly the most practical. The second technique is of greater value in studying the details of the reaction and the influence of the key reaction variables. A large number of process variables are possible including the coupling agent, the pigment, the temperature, the pressure, the time, the introduction of water or other reactive material, and, perhaps, temperature cycling. Clearly, these variables could not all be examined systematically, and it will be clear in the discussion to follow that the approach was quasiempirical, attempting to develop a satisfactory treatment in the minimum possible time.

In studies of the deposition of coupling agents using a carrier gas, the procedure used was to alternate the coupling agent treatment with a treatment using water vapor. Figure 1 shows typical results where two cycles of SiCl_4 or TiCl_4 and water vapor are used on the sample. In these studies, the sample was in the form of agglomerates, and the screening test was used to determine the strength increase. The

Table 5

STRENGTH OF TREATED ZINC OXIDE SAMPLES

<u>Coupling Agent</u>	<u>Trade Name</u>	<u>Vickers Hardness</u>
None (exposed to xylene only)		36
Tetraoctyloxy titanium di(dilaurylphosphite)	OTDLPI-46	41
Titanium di(dibutylpyrophosphate)oxyacetate	GTDBPP-158DS	44
Tetraisopropyl di(dioctylphosphito)titanate	TTOPI-41B	86
Tetra(2,2 diallyloxymethyl-1-butenoxy)titanium di(ditridrcyl)phosphite	TTMDTP-55	66
Isopropyl, tri(dibutylpyrophosphato)titanate	TTBPP-58CS	12



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FIGURE 1 FRACTION OF TiO_2 RETAINED ON #32 MESH SCREEN

(a) After 30 min SiCl_4 treatment at temperature T

(b) After 30 min TiCl_4 , or after treatment with no coupling agent in the gas stream (blank)

parameter varied was the temperature of treatment, and it is observed that, above 200°C, effective strengthening of the flocs has occurred. The curve does not clarify the effect of the coupling agent below 200°C. Presumably, the adsorbed water at this low temperature acts as a reasonably effective bridging agent and the agglomerates are strong. Above 200°C, dehydration normally weakens the agglomerates, but the addition of SiCl_4 restores or increases their strength.

More stringent tests using glass beads confirms that the SiCl_4 is ineffective in strengthening the agglomerates below 200°C. No significant improvement in strength with TiCl_4 is observed in these studies. Thus, in all later work, reported below, SiCl_4 is the coupling agent studied.

The results obtained in measurements with the pellet first evacuated, then exposed to SiCl_4 vapor, were similar to those found when a carrier gas was used. In these studies, ZnO (NJZ-SP-500) was used as the pigment because stronger pellets were obtained initially with ZnO than with TiO_2 . The influence of several parameters was examined with this experimental technique, and many of the more recent results are summarized in Table 6. For example, we can consider the influence of temperature. With the blanks (Samples 19 and 26), there seems a slight increase in strength with a temperature above 200°C, but (compare Samples 16-18 with 27-28) the strengthening is much more substantial if a small aliquot of SiCl_4 is admitted.

As an aluminum hydroxide or silica coating is normally present on pigment materials for stability, tests were made with such coatings on the ZnO pigment. A comparison of the hardness of Samples 34 and 35 indicates again the substantial improvement as the treatment temperature is made greater than 200°C.

The results of Figure 2 indicate why the high temperature is preferable. These curves are chosen because they show results where no

Table 6

HARDNESS TESTS ON ZnO PELLETS AFTER EXPOSURE TO SiCl_4 TO INDUCE INTERGRANULAR COUPLING

Sample	Coating	(a)	Temperature, °C		Pressure (torr) SiCl_4 Admitted	Hardness (L)		Remarks
			Outgas	Treatment		Before Steam (c)	After Steam (d)	
16	-	-	210	210	1.0	54	100	SiCl_4 all consumed
17 and 18	-	-	215	215	0.12	54-56	60-62	SiCl_4 all consumed
19 and 20	-	-	200	200	-	40-41	-	200° BLANK
21 and 24	-	-	350	350	220	80-120	200-230	Exposed 15 min
26	-	-	350	350	-	54	-	350° BLANK
27 and 28	-	-	350	350	1.0	76	-	-
29	Al(OH)_3	410	410	410	13	184	140	-
31	Al(OH)_3	410	410	410	-	66	52	Al(OH)_3 BLANK
32	$\text{Al(C}_2\text{F}_5)_3$	410	125	0.25	10	-	-	-
33	Al(OH)_3	400	250	2	46	-	-	-
34	$\text{SiO}_2 \cdot (\text{H}_2\text{O})_x$	250	250	1.2	58	-	-	No gases remain
35	$\text{SiO}_2 (\text{H}_2\text{O})_x$	418	418	3.0	150	-	-	SiCl_4 consumed, but HCl , etc., evolved
37	$\text{SiO}_2 (\text{H}_2\text{O})_x$	400	400	220	108	-	-	SiCl_4 treatment after pressing pellet
38	$\text{SiO}_2 (\text{H}_2\text{O})_x$	400	400	220	44	-	-	SiCl_4 treatment before pressing pellet

(a) 2 monolayers precipitated onto pigment, by standard pigment manufacturing techniques, before pressing pellet.

(b) Vickers hardness, Diamond pyramid hardness number.

(c) Readings after removal from vacuum system.

(d) After sample had been exposed for several hours to steam at 60°C.

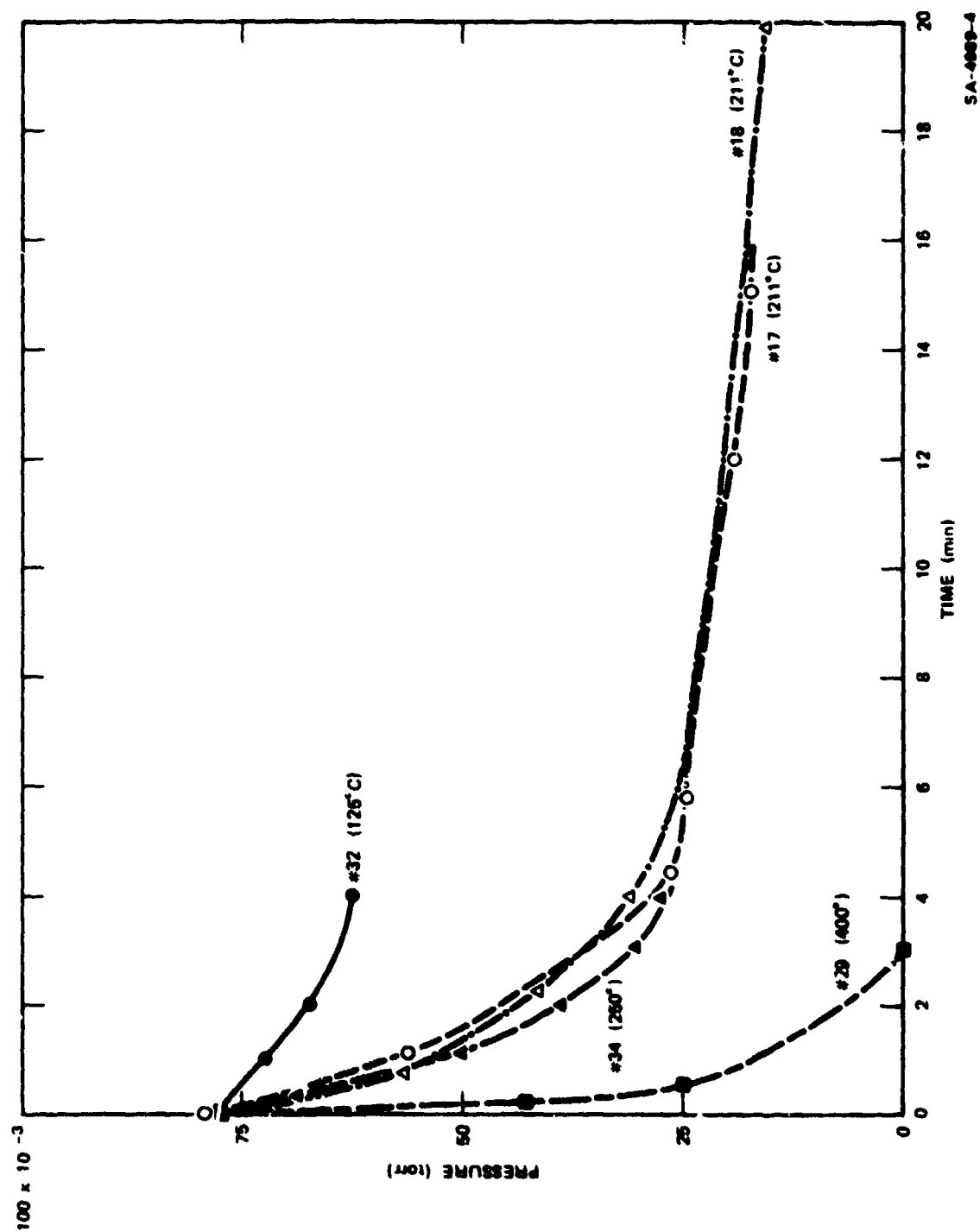


FIGURE 2 RATE OF PRESSURE DECREASE WITH TIME

0.1 torr corresponds to about 0.05 monolayers. Detailed treatment of various samples given in Table 6.

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product gases appear, and thus the rate of SiCl_4 consumption can be easily monitored. It is seen that the consumption of SiCl_4 at 400°C is relatively rapid. A comparison between samples 34 and 35 with respect to gas evolution reconfirms the picture. The release of HCl , determined mass spectrometrically, only occurs for Sample 35. As the desired interaction of SiCl_4 with OH surface groups should yield HCl , it is possible that with Sample 34 (250°C), the SiCl_4 consumption represents simply adsorption, and for the strong reaction the more elevated temperature 400°C is required.

The conclusion from the measurements of Table 6 is that effective and rapid cementing of chains of silica-coated ZnO should be realized at a temperature the order of 400°C , with the coupling agent SiCl_4 introduced from the gas phase.

B. Chain Flocculation in a Liquid Suspension

1. Flocculation by Zeta Potential Control

a. Measurement of Zeta Potential

The close relationship between electric charge on pigment particles and flocculation of their dispersion in aqueous⁴⁻⁶ and non-aqueous⁷⁻¹³ media is well established. Because our goal has been to control flocculation, it was considered desirable to control the charge on the particles. The charge originates from an electrical double layer at the surface of the pigment caused by preferential adsorption of cations or anions and by dissociation of surface molecules (e.g., dispersant). The magnitude and sign of the double layer is measured by the zeta potential, which according to the Huckel equation,

$$\zeta = 6\pi\eta u / e$$

is a function of η and ϵ , the viscosity and dielectric constant of the medium, and u , the electrophoretic mobility (velocity of the particle under unit potential gradient).

The zeta potential was measured in both nonaqueous and aqueous media. The nonaqueous medium is probably of greater significance, because we would like to initiate chain flocculation in a solvent compatible with the binder resin, e.g., methyl ethyl ketone (MEK) for fluoropolymers. To determine zeta potential, we measure the electrophoretic mobility of the particles by microscopic examination. Our first electrophoretic cell was very simple and consisted of a microscope slide with a cylindrical well that contained the pigment slurry and that was covered with a thin, glass cover slide. This cell was suitable for measurements in an aqueous medium, but it was not suitable for nonaqueous media, because the organic solvents evaporated at the interface between the cover slide and the microscope slide. The resulting movement of the liquid media interfered with the electrophoretic measurements.

To eliminate solvent evaporation, we constructed a closed cell similar to that used by Mc Gown et al.¹⁰ This cell consists of an optical path of depth 1 mm, height 10 mm, and length 50 mm. Angled side-arms, terminating with female ground-glass joints, were fused to the ends of the cell. Platinum wires were fused into male ground-glass joints, forming stoppers for the side arms. The microscope was supported in a stand at a 90-degree angle to its normal working position so that any sedimentary deposit accumulated out of the field. The illuminator was fitted with filters to remove infrared light, which may cause thermal stirring, and to remove ultraviolet light (< 4700 nm), which may cause electronic excitation of the pigment particles.

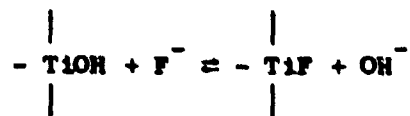
Electrophoretic mobilities were measured on some of the suspensions of pigments for which settling times were measured.

Theoretically, particles with a high mobility (i.e., high zeta potential) can be expected to produce stable suspensions, with a long time for setting. Table 7 gives the comparative results of mobility and settling time. For the electrophoretic studies, the concentrated pigment suspensions from the settling studies were diluted with dry MEK. We verified that true electrophoresis was being measured by obtaining a linear relationship between the applied electric field (which did not exceed 70 volts cm^{-1}) and the electrophoretic mobility.

In the case of ZnO, different coupling agent produce an appreciable spread in the values of the settling time, but the electrophoretic mobility values do not show the expected corresponding spread. The settling times for ZnO of > 30 and > 180 min indicate merely that settling to 1.8 ml was incomplete during the specified time; the value > 30 might possibly have been > 180, if the operator had waited long enough. For the remaining pigment samples, the values of mobility and settling time are not remarkably different in their spread.

b. The Effect of Additives on Flocculation

Flocculation can be controlled by the surface double layer (essentially the zeta potential) and such double layers can occur in aqueous suspensions by adjusting pH and by adding exchangeable ions, such as fluoride ions. The ion exchange on TiO_2 will occur with the hydroxyl groups of the pigment surface as follows:



The position of the ion exchange equilibrium will strongly depend on the concentration of fluoride and on the pH.

Table 7

COMPARISON OF ELECTROPHORETIC MOBILITY (u)
AND SEDIMENTATION TIME (t) FOR SEVERAL
PIGMENTS IN NONAQUEOUS MEDIA

Pigment	Reference (NB 657)	Solvent ^(a)	Coupling Agent	$u^{(b)}$ $\frac{\text{sec}^{-1}}{\text{V cm}^{-1}}$	$t^{(c)}$ (min)
ZnO	4-4	MEK	$\text{ClCH}_2(\text{CH}_3)_2\text{SiCl}$	24	5
	4-6	MEK	TTS	18	> 30
	8-1	MEK (dry)	$\text{ClCH}_2(\text{CH}_3)_2\text{SiCl}$	26	> 180
SnO_2	5-1	MEK	None	27	2
	5-6	MEK	TTS	31	5
	8-3	MEK (dry)	$\text{ClCH}_2(\text{CH}_3)_2\text{SiCl}$	38	2
TiO_2	6-1	MEK	None	26	2
	8-5	MEK (dry)	$\text{ClCH}_2(\text{CH}_3)_2\text{SiCl}$	38	6

(a) MEK = methyl ethyl ketone; dried over CaH_2 .

(b) All particles negatively charged, i.e., moved to the anode.

(c) Time for pigment in 10 ml of slurry to settle to about 2 ml.

We have examined the effects of ion exchange on the flocculation properties of TiO_2 by two techniques: optical microscopy, to observe the shape of the flocculates, and electrophoresis.

Microscopic examination of chain flocculation was made on some aqueous suspensions of TiO_2 (chloride-processed pigment with about 0.1 monolayers of surface alumina) as a function of suspension pH (3 and 12) and amount of fluoride ion (0 and 0.1 mmoles/g TiO_2) applied to the TiO_2 at the given pH. These pigments were dispersed with the aid of an ultrasonic generator. By use of an optical microscope (xl30), the state of flocculation of the pigment particles was examined in suspension and after drying on a glass slide.

The results show that the pigment flocculated much more in a concentrated suspension (2 wt%) than in a more dilute suspension (0.2 wt%). Chain flocculation appeared to be present in samples of the dried, concentrated suspensions. The shape of the flocs depended on the fluoride and pH pretreatment of the pigment. In the absence of fluoride, finer chains were produced for pigments prepared at pH 3 (20 x 50 μm) than at pH 12 (30 x 130 μm). The nominal diameter of the pigment particles is 0.2 μm . For pigments treated with fluoride (0.1 mmoles F^-/g TiO_2) the flocs became larger, but they were more chain-like for pigments prepared at pH 12 (40 x 130 μm) than at pH 3 (100 x 200 μm).

Electrophoretic measurements were made on the four pigments suspended in water. The particles were charged negatively for the pigments prepared at pH 3 and positively for the pigments prepared at pH 12. Fluoride did not have much of an effect on either the sign or magnitude of the electrophoretic mobility. However, these results may not have been reliable, because the suspension used for the electrophoretic measurement was very dilute, and the final pH could have been dominated by the pH of the water.

Some evidence that slow flocculation leads to chain flocculation, as predicted by theory, was obtained in preliminary experiments on the flocculation of TiO_2 in anhydrous cyclohexane. The cyclohexane was dried with metallic sodium, and the flocculation of the TiO_2 became very slow. Under these somewhat ill-defined conditions, the flocs developed in chain form. This very preliminary observation may suggest a direction for later, more detailed study.

2. Flocculation in an Electric Field

a. Theory of Field-Induced Chain Flocculation

To assist in the design of cells for field-induced chain flocculation, we need analytical models of the process. The two general techniques for chain formation that will be examined and compared are first chain formation in a uniform electric field and second chain formation at a knife-edge electrode or a fine wire.

Chain Formation in a Uniform Electric Field--The field between two parallel plate electrodes is given by

$$E_0 = V/d \quad (1)$$

where d is the spacing, V the applied voltage. A particle of high dielectric constant distorts the electric field in its neighborhood, and this distortion attracts a second particle, initiating chain formation.

The field near a conducting particle of radius a in an insulating medium is given¹⁴ by

$$E = E_0 \left(1 + 2a^3/r^3 \right) \quad (2)$$

where r is the radial distance from the particle, and for simplicity we consider only $\theta = 0$, where θ is the angle between the radial vector and the electric field. The charge on the surface of a conducting spherical particle of radius a in a field E is given approximately by

$$\sigma = 4\pi K \epsilon_0 E a^2 \quad (3)$$

where K is the dielectric constant (100 for TiO_2) and where the separation of charge is taken as equal to the radius a . Equations (2) and (3) are slightly different in form if the particle is nonconducting (with a high dielectric constant) but for our approximation the difference can be neglected.

Now the energy of a particle having an induced dipole with charge separation a in a field is given by

$$U = \sigma E a \quad (4)$$

and the force by

$$F = \partial U / \partial r \quad (5)$$

Combining equations (1) through (5), we have that the force on a particle due to the field distortion caused by a nearby particle is

$$F = 48 \pi K \epsilon_0 E^2 (1 + 2a^3/r^3) a^6/r^4 \quad (6)$$

By Stokes Law, the velocity of a particle v due to such a force (here the velocity of two pigment particles toward each other) is given by:

$$v_0 = F/6\pi\eta a \quad (7)$$

If, for example, the viscosity η is 1 poise as in a typical solvent, and the mean separation of the particles [r in Equation (6)] is $10\ \mu$, we have from Equation (7)

$$v_o \sim 2.4\ \mu/s \quad (8)$$

where we have taken $a = 0.5\ \mu$, $E_o = 10^7\ \text{V/m}$, and $K = 100$. With these values one could expect the particles to coalesce and could expect chain flocculation.

On the other hand, with a more dilute slurry the mean separation increases, and the velocity v_o decreases, from Equations (6) and (7), as r^{-4} . Thus, if $r = 50\ \mu$, the particle velocity leading to flocculation is lower by almost a factor of 1000, and flocculation will not occur.

Chain Formation at a Wire or a Knife-Edge Electrode--In estimating the field at a wire or a knife edge, we use the formula for the field between two concentric cylinders, an inner cylinder of radius r_1 (in our case the radius of the wire or knife edge), and an outer cylinder of radius r_o (the counterelectrode). The field at distance r from the center of curvature of the wire or knife-edge is then given approximately by

$$E = V/2\pi r \log (r_o/r_1) \quad (9)$$

A spherical pigment particle in this field, from Equations (3), (4), and (5), will be subjected to a force at a distance r of:

$$F = (a^3/r^3) \{K\epsilon_o V^2/\pi(1\epsilon; r_o/r_1)^2\} \quad (10)$$

and with $\log(r_o/r_1) \sim 5$, we have from (7) the velocity of particles in a liquid medium is given by:

$$v_o \cong 200 \mu/s$$

where $a = 5 \times 10^{-6}$ m, $r = 100 \mu$.

Thus, in a few seconds all particles within 100μ m of the knife edge will be attracted to the growing flocs.

In the case of an electric field applied to a wire in an aerosol, the pigment particles are in a medium of viscosity about 2×10^{-4} poise, so the particles will be swept to the wire from a greater distance than in the case of a liquid medium. We will assume a particle in the aerosol, moving parallel to the wire under the influence of the following gas, spends a time $t_o = 1$ second in the neighborhood at the wire. To collect all particles within a distance r_{max} , the field at the distance r_{max} must be great enough to impart the velocity v_o' where

$$v_o' = r_{max}/t_o \quad (11)$$

$$= r_{max}$$

to the particles.

From Equations (1) and (7) we have that the terminal velocity imparted to the particles at distance r_{max} as given by

$$v_o' = (6\pi\eta a)^{-1} \cdot (a/r_{max})^3 \cdot \{K\epsilon_o V^2 / \pi(\log r_o/r_1)^2\} \quad (12)$$

Equating (11) and (12), with $\eta = 2 \times 10^{-5}$ decapoise for air, $V = 10^4$ volts, $K = 1$, and the other values the same as above, we find

$$r_{\max} \sim 1 \text{ mm}$$

(13)

suggesting that if a particle comes within about 1 mm of the wire, it will be incorporated into the growing chains.

Conclusions from these Calculations--For the case of a uniform electric field it appears that initiation of chain flocculation is only practical with a dense slurry. In our studies to date, where a thin slurry has been used to facilitate observation, chain flocculation in a uniform field has been unsuccessful, and the calculations indicate why.

The knife-edge or the wire approach is more effective because the field varies as r^{-1} compared with r^{-3} in the homogeneous field case. Thus in these cases the particles are affected by the field inhomogeneity over much larger distances from the site of chain formation.

b. Experimental Observations with a Liquid Suspension

Chain flocculation of TiO_2 was examined in these studies. A priori, it should be the pigment most amenable to chain flocculation in an electric field, because of its high dielectric constant. Several geometries for cells in which to induce chain flocculation from a liquid were examined. Of most interest are those involving a uniform electric field and those involving the electric field at a knife-edge (or point).

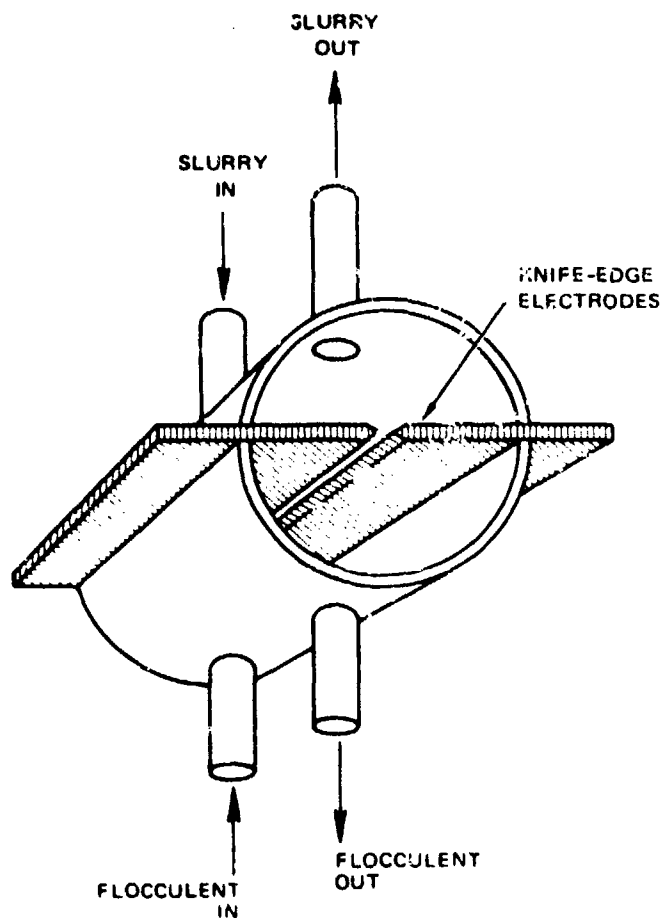
Attempts to date to induce chain flocculation in a uniform electric field have been unsuccessful with either ac or dc fields and with various solvents. The reason for the lack of success with a homogeneous field is discussed above under theory. However, the theory suggests that there may be advantages to flocculation in a uniform field if the technique can be made successful, because more accurate chain formation may be possible. Also there may be advantages in scaling up.

We have succeeded in inducing chain formation at a knife edge electrode. The preferred solvent is cyclohexane. Benzene has also been used successfully. No success has been observed in MEK, presumably because of its larger dipole moment, but also possibly because of an unknown zeta potential effect. Alternating voltages seem preferable, although with the cyclohexane solvent, success was sometimes obtained with a dc field.

Figure 3 shows the flocculation cell tested. The knife-edge electrodes are simply stainless steel razor blades. The ends of the cell, shown open for clarity, are of course closed, and the four inlet and outlet tubes are the only ports.

In measurements to date, a TiO_2 slurry was introduced, passed through a 1-mm slit, and the formation of chains at the slit was observed visually. Figure 4 shows results in an ac field indicating the voltage range of interest. The TiO_2 was dispersed by the deflocculant Aerosol O.T. (1/4 monolayer). The ordinate gives the time necessary to form chains of TiO_2 about 0.25 mm in length; the abscissa shows the voltage applied (60 Hz). It was observed that a too high voltage caused turbulence in the slurry and destroyed the chains. Thus, there is an optimum intermediate voltage (field) for rapid chain formation. At voltages below this optimum, the chains were finer, which is a desirable feature for our purpose. Presumably, therefore, a voltage lower than that corresponding to the maximum rate will be found most desirable. All the variables have not been identified, and farther work is necessary to make the technique completely reproducible.

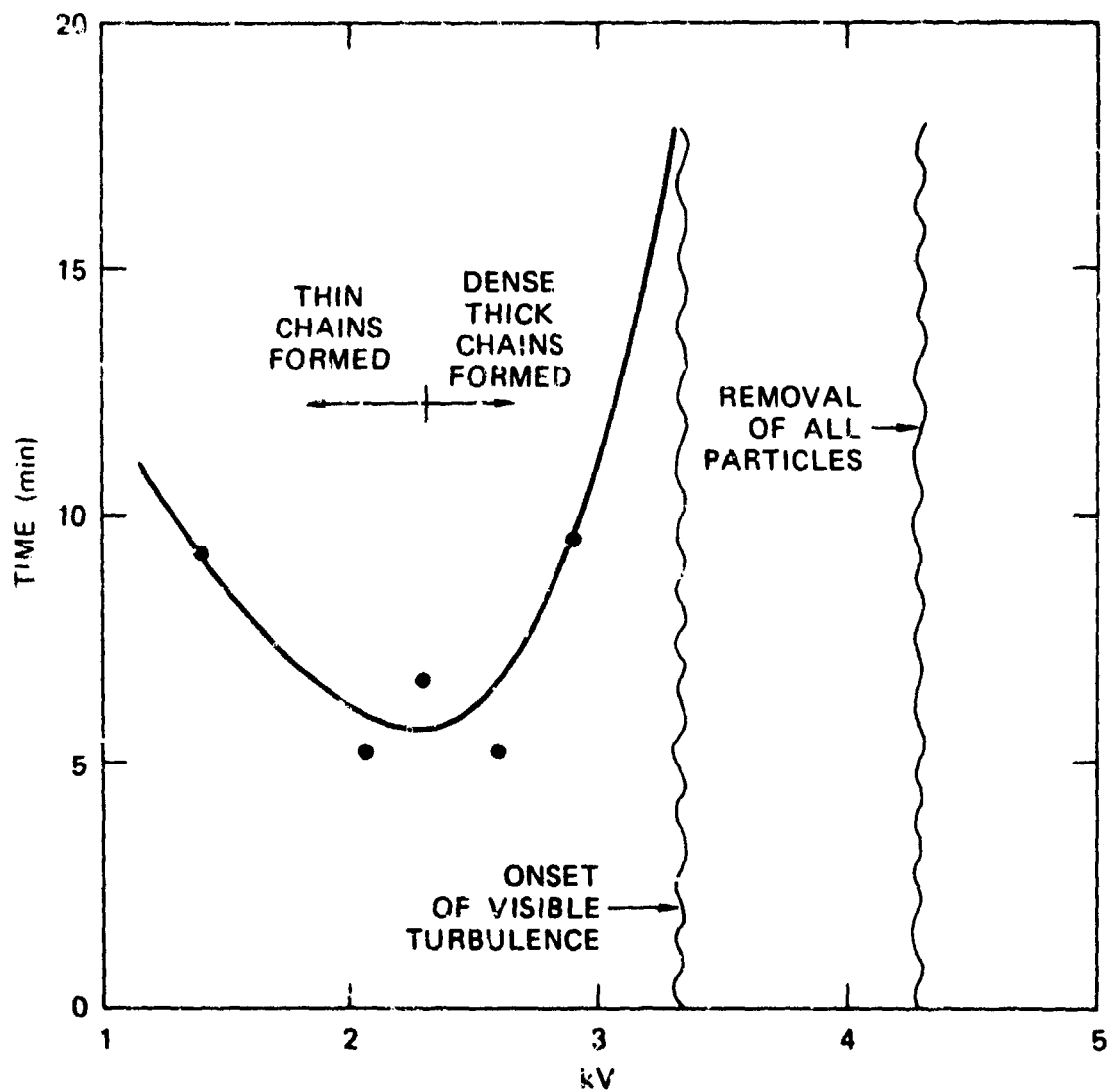
In the experiments to date we have used only two ports of the cell. As indicated in Figure 3, the cell is designed with two extra ports to permit the introduction of additives coupling agents. Such additives, as discussed in Section A3 above, are introduced to form interparticle bridges and stabilize the chains once they are formed.



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FIGURE 3 APPARATUS FOR FORMATION OF CHAIN FLOCCULENTS

End of tube shown open for clarity, but is sealed in practice.



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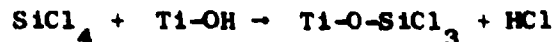
FIGURE 4 TIME TO FORM 0.5 mm CHAINS ON METAL KNIFE
EDGE AS FUNCTION OF APPLIED VOLTAGE (60 Hz)

C. Generation of Chain Flocs from an Aerosol

1. Apparatus Development

An apparatus was designed to provide pre-formed flocs suitable for introduction into a vehicle, where the flocs are induced by an electric field in an aerosol and are cemented by being exposed to SiCl_4 . The concept involves the use of the high electric field associated with a fine wire. Because pigment particles are carried as an aerosol past this wire, the pigment is deposited in the form of chains. The wire is heated to a sufficient temperature ($> 400^\circ\text{C}$), and the coupling agent SiCl_4 is introduced, and the chains are, thus, cemented into permanent flocs.

Figure 5 is a schematic diagram of the preliminary apparatus for chain floc generation. Most of the results discussed below were obtained with this system. The essential parts are: a high-voltage ac source that generates a high field near a 3-mil wire in the reactor; a heater supply that heats the wire, permitting the silane bridging reaction, a source of SiCl_4 ; and a mechanism to provide a fine aerosol of the pigment. The pigment particles, attracted to the wire by dielectrophoresis action,¹⁵ form chains because an approaching particle moves to the end of an existing chain where the field is highest. The SiCl_4 interacts with the pigment surface, and as the pigment is heated by the hot wire, the following reaction goes to completion:



If one SiCl_4 molecule interacts with OH groups on adjacent particles, the bridging or cementing of the particles is effected.

Two major problems were encountered with the apparatus shown in Figure 5. First, it was determined that the best way to remove the

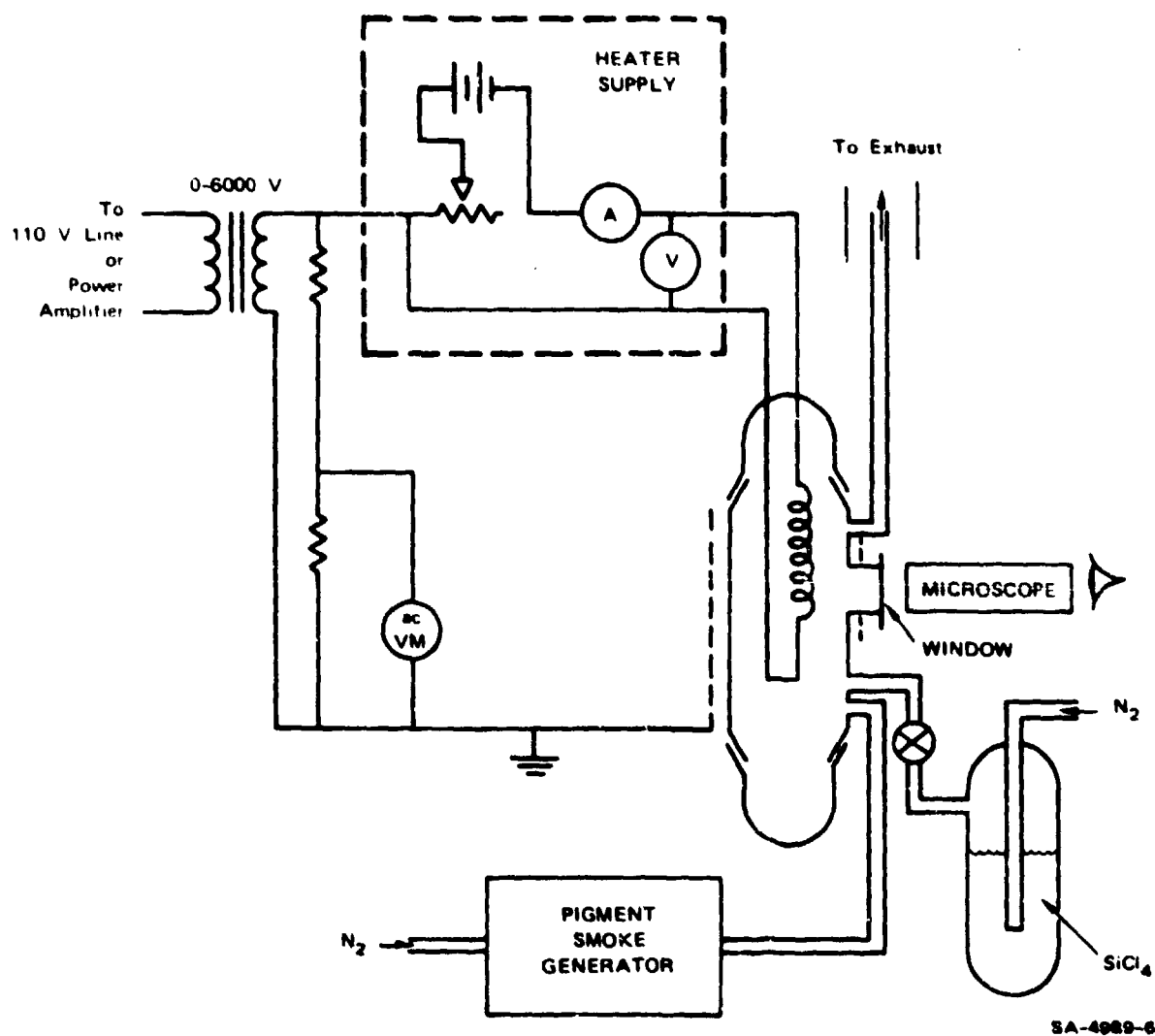


FIGURE 5 APPARATUS FOR FLOCCULATION OF CHAINS FROM AN AEROSOL

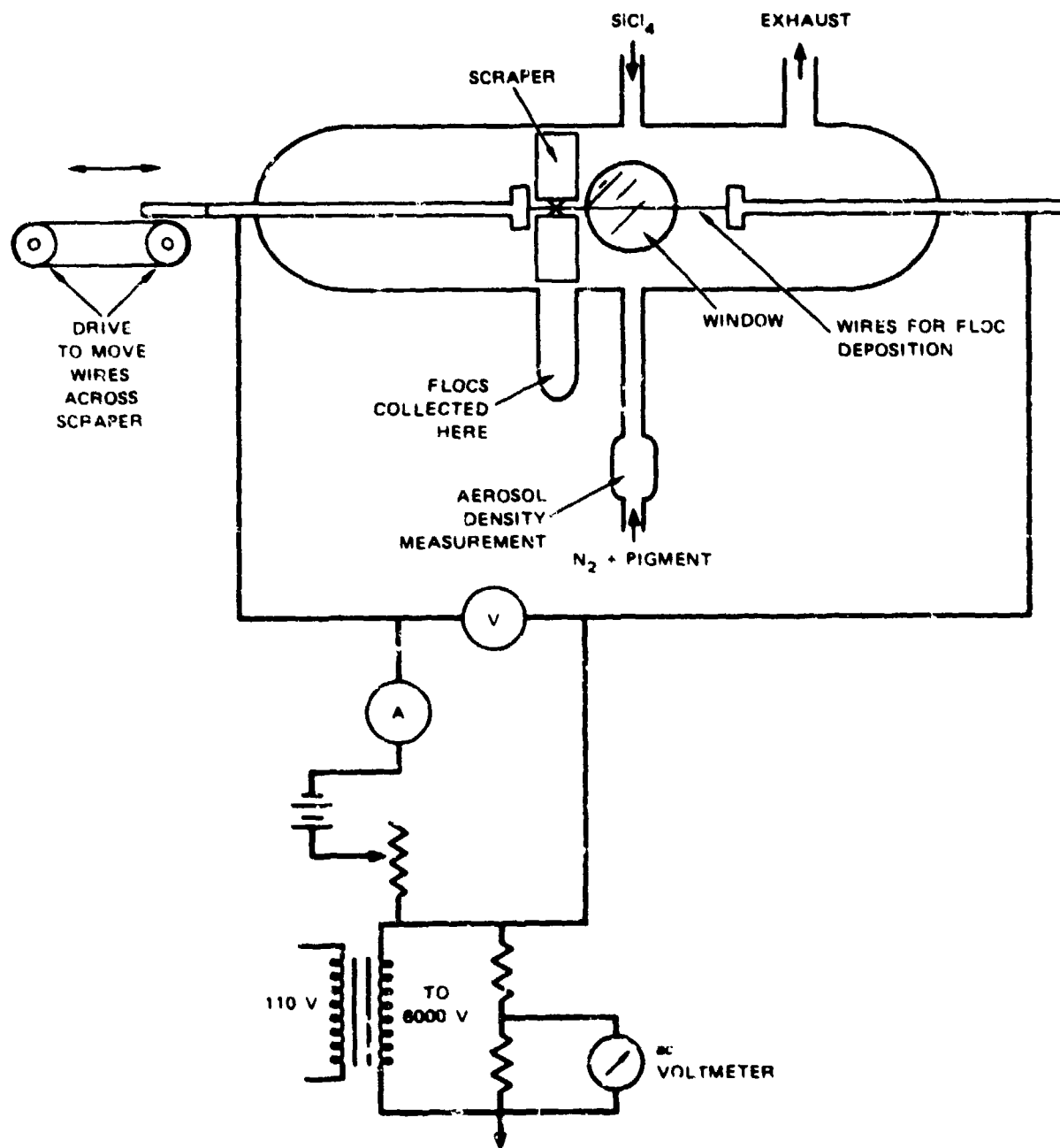
chains was by mechanically scraping them from the wire. However, such a process is tedious with that design. Second, it became clear that to accumulate reasonable quantities of pigment, it would be necessary to cycle the process. Thus, to avoid excessive delay, an automated process is required.

Figure 6 shows the redesign of the system to permit automatic operation. The electrical features are unchanged from Figure 1, except that a 6-wire wand is used rather than a single wire. The important change is the inclusion of a unit to move the wires through a scraper, and a flask under the scraper to collect the pigment particles. In addition, a light-scattering module has been included for measurement of the osol density, permitting better control of the process.

The wand will be positioned for one-half cycle in the reaction chamber where the chain flocs will be produced. In the second half cycle, it will be moved across the scraper to collect the pigment and then be returned to the reaction chamber. With optimum floc growth, calculations (see below) indicate a few thousand cycles per gram will be required for pigment generation with this simple design.

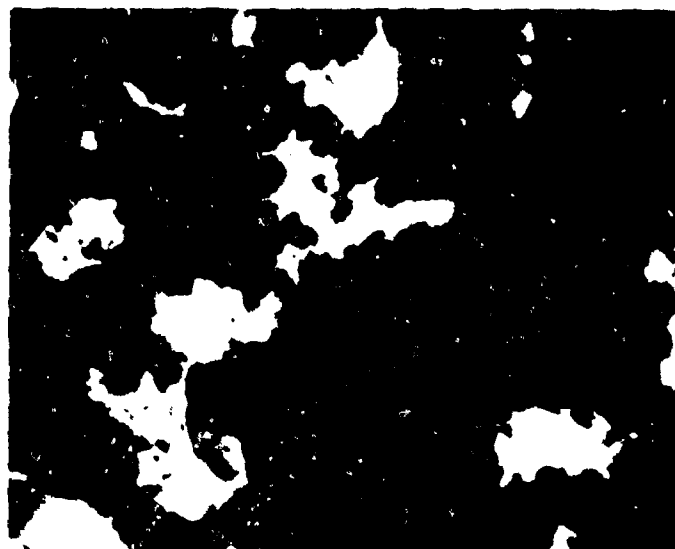
2. Results

Photographs of chains and flocs are shown in Figure 7. The flux of pigment particle was about 10^{-3} g/min. The upper photo shows particles prepared early in the period using a platinum wire at 1500 V; the particles were removed from the wire by scraping onto a glass slide. The lacework texture is clear, but, apparently, during the scraping the chains folded into themselves. In theory, they should unfold when introduced into a vehicle together with a dispersing agent. The lower photo shows flocs prepared on a nichrome wire at 3000 V. Because of a limited depth of field, only a few of the flocs are in focus; and even in those cases, because each floc has a tree-like structure, parts are



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FIGURE 6 AUTOMATION OF FLOCCULATION APPARATUS



(a) TYPICAL 10nm FLOCS ATTACHED TO THE WIRE



(b) FLOCS AFTER REMOVAL BY BRUSHING. THE LIMITED DEPTH OF FIELD LEADS TO PARTS OF ALL THE FLOCS BEING OUT OF FOCUS

SA-4989-7

FIGURE 7 FLOCS OF TiO_2 INDUCED BY AN ELECTRIC FIELD

out of focus. The length of the structures is about 10 μm . Figure 8 shows an electron microscope picture of a floc (magnification 20,000) prepared on the apparatus of Figure 6 at 5000 V.

In the development of the technique many general observations were made and the rest of this subsection describes these. It was determined that the wire temperature must be about 900°C to obtain a pigment temperature of greater than 400°C, the temperature (as determined experimentally, see Figure 2) required for rapid bridging. The pigment temperature was estimated by the depth of color of the TiO_2 . (TiO_2 becomes an increasingly strong yellow as the temperature rises.)

It was found that the electric field (the applied voltage) is at an optimum value at some intermediate magnitude. The observed behavior suggests that if the field is too low, the collection of particles is not influenced by the field, and if the field is too high, the trajectory of the particles is unaffected by previously adsorbed particles. In either case, the particles become deposited randomly, and, in the case of a high field, the particles form a uniform coating over the wire surface. The region of 1 to 3 kV on a 3-mil wire seems satisfactory for chain formation. More recent results (see below) using conductive pigments show that with such pigments much higher voltages can be used while still obtaining chain formation.

Most of the work was performed using a platinum wire; this was chosen because we considered that the more noble metal, with no oxide present, would form weaker bonds to the silane and, hence, allow easier removal of the pigment. However, in later studies we have used nichrome because of the poor mechanical strength of platinum at 900 to 1000°C. Superior chain formation that was less dependent on voltage and aerosol density was observed with the nichrome. The reason for the better results is not clear.



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FIGURE 8 ELECTRON MICROGRAPH OF A CHAIN FLOC
Magnification 20,000x

Methods of removing the flocs from the wire were examined. We have tested heat, high fields (ad and dc), ultrasonic vibration of the wire (both in gas and in an aerosol environment), various gases such as H_2O and HCl , and the use of a ribbon rather than a wire. None of these methods proved effective. Thus, we have adopted the technique of mechanically removing the flocs by brushing or scraping, incorporating the process in the design of the "automated" device of Figure 6. However there has been some indication in recent experiments, reported in the next section, that under certain conditions a dc field can be used to remove the flocs.

The mechanical removal of the flocs from the wire must be done with care to minimize crushing of the flocs into spheres. Such crushing is observed with a "dull" scraper, and it may be deleterious--we have not determined whether the structure damage is reversible. In experiments using a ceramic scraper, such damage to the floc structure were observed and interpreted as due to crushing at the dull edge. A sharp metal scraper was used to remove the flocs shown in Figures 7 and 8, maintaining their open structure during removal.

To a first approximation, both the length and the total volume of the chains increases as the square of the applied voltage. Thus with 7 kV applied, well-resolved chain formation is still observed with chains the order of $150 \mu m$ long. The high-voltage chains are heavily branched at the top, narrow near the wire; their shape resembling that of an oak tree. We estimate from this data that with the semi-automated apparatus we can produce about 3 mg per pass; that is we will produce chains at the rate of 1 gram per 300 cycles.

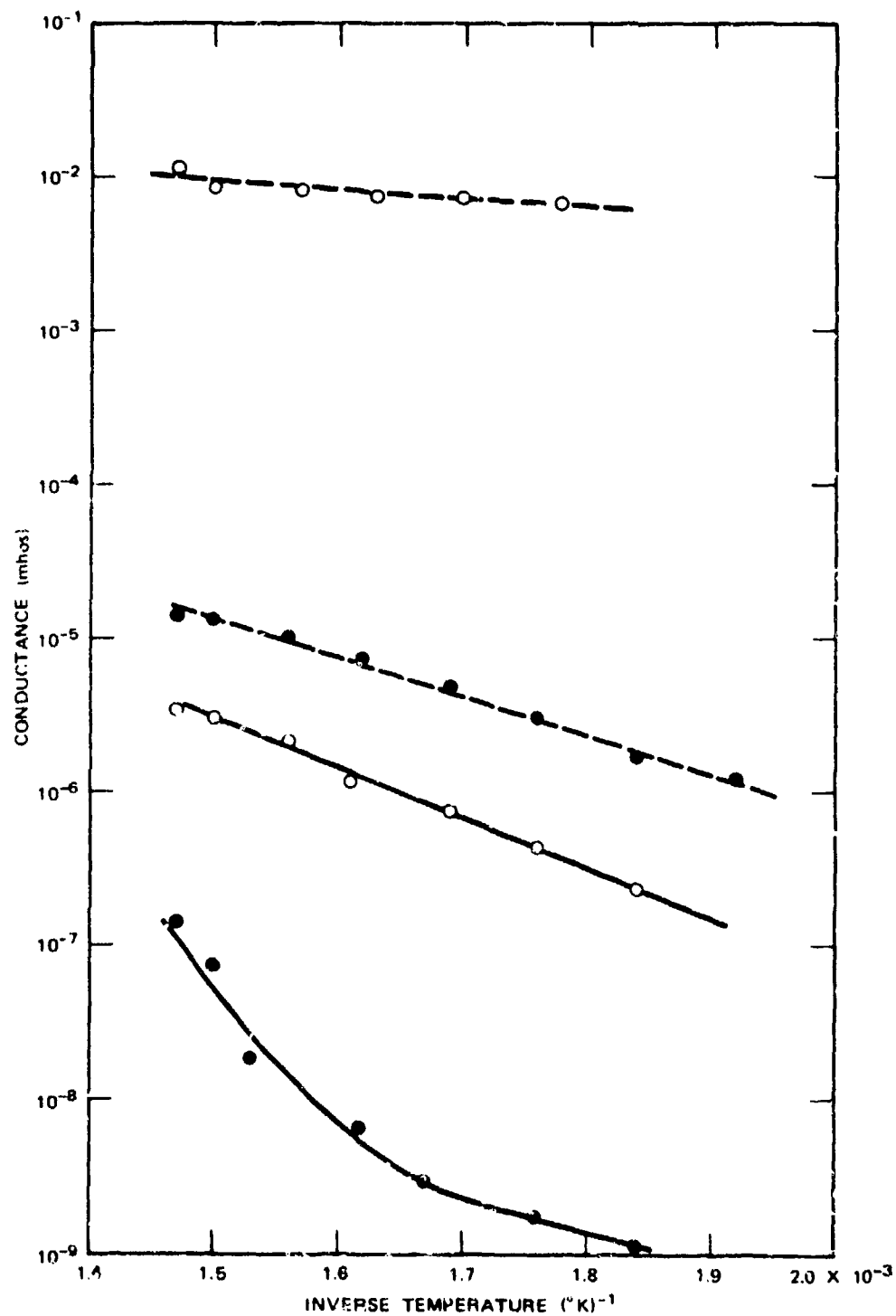
D. Preparation and Flocculation of Conductive Titanium Dioxide

1. Electrical Properties of Bridged Pigment Particles

It is found, surprisingly, that the use of SiCl_4 to cement pigment particles together actually increases the intergranular conductance. This is simply shown in pressed-pellet experiments, illustrated in Figure 9. The pressed pellet is initially evacuated at 400°C to desorb adsorbed oxygen, thus enabling satisfactory intergranular conductance. In Figure 9 the conductance temperature characteristics at this stage are indicated by solid curves. The coupling agent is added in the normal fashion, the sample re-evacuated, and it is found that for both ZnO and TiO_2 , the conductance of the pellet substantially increases (dotted curves).

It is also necessary to anticipate the effect of the SiCl_4 treatment on interfloc conductance. In the chain flocs, which are the ultimate objective of this program, it is necessary to have good electrical conductance between one chain (coated with the coupling agent), which is in physical contact with an adjacent chain, to get overall conducting paths through the final paint. The effect of the coupling agent on the interfloc conductance was tested as follows. First, the coupling agent was added to the pigment particles, then the pigment particles were pressed into a pellet in the normal fashion, and the pellet was evacuated at 400°C . It was found that the conductance of pellets where the coupling agent was deposited before pressing the pellet differed only slightly from the high conductance observed in Figure 9, where the coupling agent was introduced after the pellet had been pressed.

Thus, it would appear that, contrary to expectations, the coupling agent, silicon tetrachloride, provides a substantial improvement both to intergranular conductance and to interfloc conductance. If this characteristic is retained into the final paint with no deleterious



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FIGURE 9 INFLUENCE OF SiCl_4 TREATMENT ON INTERGRANULAR CONDUCTANCE

Solid circles: TiO_2
 Open circles: ZnO
 Solid lines: before SiCl_4 treatment
 Dotted lines: after SiCl_4 treatment

effects, it may substantially simplify the attainment of the goal of a suitably conducting white paint.

2. Preparation of Conductive Titanium Dioxide

Conducting pigments were prepared for preliminary study in the early apparatus. With TiO_2 we have found the best color (light blue) for combined high conductance and anticipated flammability resistance is obtained with Nb-doped material. To avoid an insulating surface layer, the material is best quenched to room temperature from the diffusion temperature (1000°C). Alternatively, the material can be etched lightly to remove the insulating surface layer. The insulating surface layer is presumably formed when oxygen is adsorbed ($T < 400^\circ\text{C}$) at temperatures high enough ($T \gtrsim 200^\circ\text{C}$?) for rapid electron transfer or Nb movement. This observation illustrates the problem we will have to solve in a later phase of this study, namely, the slow formation of insulating surface layers by reaction with atmospheric oxygen.

Our final recipe, with which we prepared 100-g lots of conductive TiO_2 for the studies of chain flocculation described below, includes impregnation of the powder by precipitation of NbCl_5 , calcining at 1100°C , quenching in water to room temperature, followed by ball milling.

3. Chain Flocculation of Conductive Titanium Dioxide

It was found that well-defined and well-separated chains are much easier to form (on our 3-mil wires) with conductive pigment than with the nonconductive material studied earlier. Presumably this occurs because the field gradient at the tip of a growing chain is higher if the tip is at the voltage applied to the wire (as is the case with conducting pigment), so that an approaching particle is attracted more strongly to the tip. Additionally, it was found that the growth at the tip is more continuous with tetrachloroallane present--an observation

that is consistent with our earlier observation that the silane increases the interparticle conductance.

There has been some indication that, with conductive pigment, if the chains become too long (in the absence of silane) they can be broken by the repulsive electrostatic voltage. We have not observed such rupture with an ac voltage when the silane is present to cement the chains as they grow. However, with a high dc voltage applied, there has been scattered evidence of breaking of chains even when stabilized by the tetrachlorosilane. This effect is emphasized if the wire is cooled before the application of the voltage. This, if found reproducible, may be of substantial benefit, as the technique could lead to a non-mechanical method of removing the chain flocs from the wires.

A series of studies was made comparing chain formation of Nb-doped TiO_2 on a hot (circa 900°C) wire versus a wire at room temperature. This comparison yielded results interpretable, as above, that a highly conducting pigment (the 900°C case) forms chains more easily than a poorly conducting pigment.

With the cold wire, the pigment showed a marked tendency to coat the wire, that is to deposit as an even layer. Over the whole voltage range there was a marked tendency toward improvement for the hot wire over the cold in the characteristic of chain formation, including longer chain lengths. This behavior is highly beneficial in that it permitted operation at a much higher voltage and, thus, faster rates of floc formation.

III FUTURE DIRECTIONS

Of the five steps to the development of a satisfactory coating, as outlined in the second paragraph of Section I, the first two have been completed satisfactorily and we are about half way through the third. As discussed in the introduction, we can in principle prepare an improved coating with the present flocculation methods. However, the results to date show no reason to deviate from systematic progress through these various steps as the way to produce in the shortest possible time a superior coating. Some of the investigations that will be made first are discussed in the last subsection of Section I.

As indicated in the text of this report, however, we have at each decision point chosen the most direct route to the objective. When the primary objective is realized (satisfactory conductive coatings) it may be of value to back up and test some of the other approaches indicated in the text, because some of these approaches may lead to substantial cost benefits in volume preparation of conductive coatings. In particular at this time, we can point to the possibilities of zeta potential control for direct chain flocculation, or to chain flocculation and curing by an electric field in a nonpolar solvent. These techniques for the formation of chain flocs may in the end lead to much lower cost coatings.

IV ENVIRONMENTAL IMPACT

It is clear that with the technique used in chain flocc formation, surplus aerosol and surplus SiCl_4 must be removed from the exhaust to avoid adverse environmental effects. However, it is not anticipated that such removal will be difficult because excess pigment is easily removed by filtration and/or electrostatic precipitation, and the silane hydrolyzes readily and, therefore, is removable by water treatment.

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